

Zinc-Complexes in Natural Rubber Latex Sulphur Vulcanisation System

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Zinc-complexes are essential ingredients in natural rubber latex (NRL) sulphur vulcanisation systems as they enhance the vulcanisation efficiency and improve the vulcanisate properties. Sulphur, zinc-type accelerators and zinc oxide (ZnO) are the main chemical ingredients utilised in a vulcanisation system. Zinc type accelerators accelerate the vulcanisation process in many rubber products manufacturing, while ZnO, enhances the vulcanisation efficiency. However, these chemicals may form residuals and could be released from the vulcanisates, either during the product manufacturing process or from the finished products. These chemicals may contribute towards environmental pollution, while some residuals are known to induce Type IV skin sensitivity. Thus, understanding the role of these zinc-containing chemicals in the processing of NRL based products can help the optimisation on the amount of chemicals needed for the latex products. This study showed that the amount of residual carbamate (DEC) extracted from vulcanised NRL films reduced with increased amount of ZnO content. The physical properties and crosslink densities of NRL films improved with addition of zinc diethyl dithiocarbamate (ZDEC) and ZnO. The study also confirmed the effect of heating whereby NRL films heated at high temperature demonstrated prominent differences in physical properties and residual DEC.

Keywords: zinc-containing compounds; physical properties; residual carbamate (DEC); heating

The physical properties of most rubber products during application depend on the nature of their polymer networks. On the other hand, the type and density of the polymer network depend on crosslinking and the reaction conditions during the crosslinking process. The chemicals used for this purpose in NRL products are sulphur, as the main polymer crosslinker and other chemicals functioning as accelerator and activator for the crosslinking reactions. Rubber product manufacturers prefer zinc-complexes such

as ZDEC as it is known as an ultra-fast accelerator in the presence of ZnO as the activator of vulcanisation systems. In NR sulphur vulcanisation, these chemicals have been widely described and are often associated with accelerating and enhancing the crosslink formation, thus improving the physical performance^{1–3}. Reaction of ZDEC and ZnO with sulphur forms active sulphur-accelerator complexes suitable to initiate sulphur crosslinks between polymer chains, creating mono-, di- or polysulphidic crosslinking⁴.

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Despite the importance and beneficial effects of these chemicals for product purposes, their residuals can be found in the finished products⁵. ZDEC is one of the most common chemicals responsible for skin problems (Type IV allergy)⁶. There is always a possibility that residual ZDEC, left in the products such as gloves could be eluted *via* sweating during usage. Zinc is well-known as a heavy metal component and lately, environmental issues concerning the presence of heavy metals in industrial waste is one of the main public concerns^{7–10}. Chemicals released from rubber processing to the environment influence human health as well as the ecological system.

Based on some theoretical and experimental studies, Nieuwenhuizen and others¹¹ detailed the reaction cycle of NR sulphur vulcanisation with zinc dimethyl dithiocarbamate (ZDMC). They suggested the possibility of the sulphur-accelerator complexes to degrade to zinc sulphide (ZnS) and dithiocarbamic acid at higher temperatures. The theory points towards a practical method to reduce the amount of residual accelerators by degrading the residual complexes into leachable materials that can be eliminated during

product processing thus reducing the possible Type IV skin sensitizer.

The present study evaluates the vulcanisation of NRL with the aim of minimizing the residual zinc-complexes in vulcanised NRL films.

MATERIALS AND METHODS

High ammonia (HA) latex concentrate was purchased from Lee Latex Sdn. Bhd., Malaysia. Potassium hydroxide and potassium laurate were products of System[®] Chemicals, Malaysia while other chemicals used were of commercial grades.

Dipped NRL film Preparation

Dipped NRL films were prepared using the formulation given in *Table 1* with varying ZDEC and ZnO contents. The chemicals were added in the order shown. The compounded latex was stirred for 60 min and then left to mature at room temperature for 48 h. Dipped calcium nitrate coagulated NRL films were prepared from the matured NR latex mix.

TABLE 1. FORMULATION FOR NRL VULCANISATION MIXES
(in parts per hundred rubber, p.h.r.)

Ingredients	1	2
60% HA latex	100	100
10% Potassium hydroxide	0.3	0.3
20% Potassium laurate	0.3	0.3
50% Sulphur	1.0	1.0
50% ZDEC	0–1.0	0.9
50% ZnO	0.25	0–0.5
40% Wingstay L [®]	1.5	1.5

The NRL films were leached during their gel state in a hot water bath set at $70 \pm 2^\circ\text{C}$ for 1 min. The films were further heated in a circulating air oven at $100^\circ\text{C} \pm 2^\circ\text{C}$ for 30 min, before being leached in the hot water bath for 1 min. The dipped film was then air-dried and removed from the glass former.

In an attempt to study the effect of residual ZDEC at elevated temperatures, the NRL films prepared were heated in an oven at various temperatures, ranging from 100°C to 160°C . The samples were left in the oven for 10 min up to 120 min. Films that were air dried at room temperature for 2 h were used as controls.

Azeotrope Mixture (AM) Extraction

AM consisting of 582 mL chloroform, 704 mL acetone and 548 mL methanol was first prepared. A $7\text{ cm} \times 7\text{ cm}$ test specimen was immersed in a vial containing AM at a ratio of 1:10 (1g to 10 mL). The vial was placed on a shaking platform and was continuously shaken at a rate of 200 revolutions per minute (r.p.m.) for 3 h under ambient conditions. The test specimen was removed and the AM in the vial was dried overnight in a fume cupboard followed by a final drying in a vacuum oven at $55 \pm 2^\circ\text{C}$ with the residual of the extract remaining in the vial.

High Performance Liquid Chromatography (HPLC) Analysis

The dried residual from the extraction process was redissolved in 5.0 mL chloroform and mixed with 1.7 mL copper sulphate solution (1M). It was then shaken to form the respective copper dithiocarbamate (CuDEC) complex^{12,13}. The complex formed was quantified by the HPLC method. The instrument used was a Waters HPLC equipped

with a C_{18} -bonded reversed phase column (3.9 micron, 150 mm) with detection at a UV-wavelength set at 269 nm. The gradient mobile phase used was acetonitrile and water at a ratio of 90:10 (v/v) with a 1.0 ml/min flow rate.

Physical Testing and Crosslink Density Determination

The tensile properties were determined according to *ISO 37*. Determination of crosslink density was done *via* the equilibrium volume swelling method, where the test specimen was weighed and immersed in toluene in a swelling bottle and left under an ambient temperature of $25 \pm 3^\circ\text{C}$ for 48 h. The swollen test piece was then removed and the excess toluene on the surface was quickly blotted off using filter paper. The swollen sample was weighed in a closed weighing bottle. The sample was then dried until constant weight. The crosslink density was determined by the Flory-Rehner equation¹⁴

$$-\ln(1-V_r) - V_r - \chi V_r^2 = 2\rho V_o n_{\text{phys}} V_r^{1/3} \quad \dots 1$$

where, ρ is the mass per unit volume of network, χ is the polymer-solvent interaction parameter, V_r is the volume fraction of rubber in swollen condition, V_o is the molar volume of the swelling agent and n_{phys} is the concentration of physically effective crosslink density.

RESULTS AND DISCUSSION

Vulcanisation process with suitable chemical ingredients improves the NRL films' physical properties. As expected, the tensile strength (TS) of the films increased drastically in the presence of ZDEC in the latex mix, justifying the need of an accelerator in the vulcanisation process. *Figure 1a* illustrates the increase in TS values with increasing

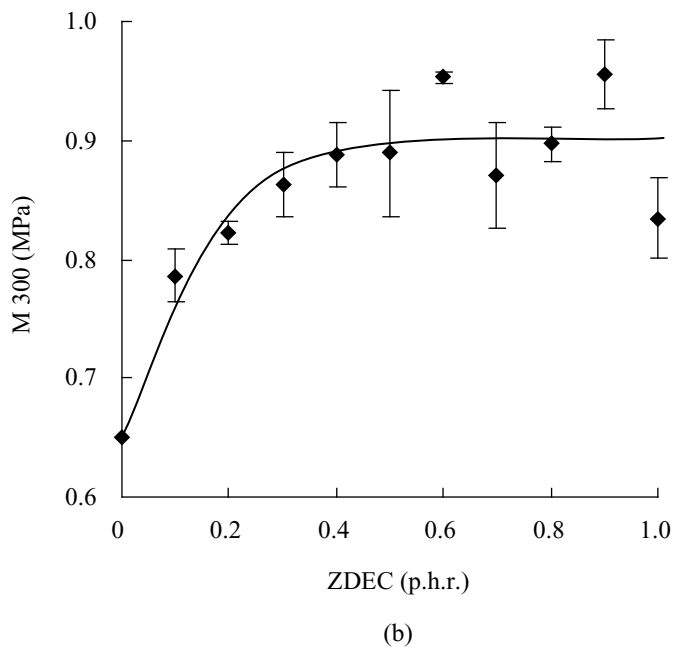
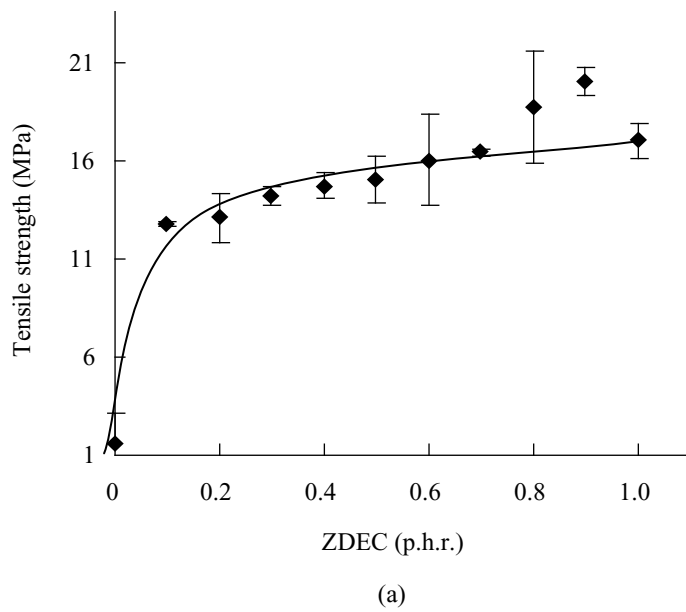


Figure 1. Effect of varied ZDEC to (a) TS values and (b) M300 values.

ZDEC content, while holding ZnO at 0.25 p.h.r. TS increased up to 0.8 p.h.r. of ZDEC before leveling off. The modulus, M300 values increased with ZDEC content (*Figure 1b*), however tended to level off above 0.4 p.h.r. ZDEC. The scattered points in M300 above 0.5 p.h.r. ZDEC are probably due to the inaccuracy of the experiment. The leveling off of the modulus value above 0.4 p.h.r. ZDEC content indicated a minimum requirement of ZDEC in the latex vulcanisation for effective NRL films' stiffness.

Crosslink density measurements were carried out to assess the importance of ZDEC in the crosslink formation in the NRL films. In *Figure 2*, the crosslink density estimated from the equilibrium swelling method showed an increment in crosslink formation with increased ZDEC content, a similar trend as in *Figure 1*. NRL films without ZDEC had a very low crosslink density, confirming the role of ZDEC in accelerating the vulcanisation process.

A plot of extracted DEC against the amount of ZDEC added into the latex mixes is given in *Figure 3*. The relationship between extracted DEC and added ZDEC was more or less linear until about 0.8 p.h.r., after which the amount of extractable DEC remained constant. The extracted DEC represented about 10%–20% of the actual amount utilised in the latex mixes. It could be that the dense crosslink formation in the NRL films above 0.8 p.h.r. ZDEC restricted the unreacted ZDEC from being extracted out. Theoretically, most of the ZDEC added into the latex mix should be recoverable, considering that sulphur vulcanisation generated mainly carbon-sulphur-carbon type crosslink network. It was found that formation of a denser crosslink occurred at high residual DEC content in the latex mixes. The extracted residual DEC however, only accounted for 10%–20% of the actual ZDEC employed probably caused

by degradation, and by the washing out that followed during the NRL films preparation while the other 80%–90% of the DEC still remained within the films.

As with the varying ZDEC contents, the TS properties of NRL films prepared from latex mixes with varying ZnO contents also showed a similar phenomena as shown in *Figures 4a* and *4b*. At a constant ZDEC level of 0.9 p.h.r. in all the mixes, the results indicated that the effectiveness of ZnO in contributing to the physical properties was no more than 0.5 p.h.r. Nevertheless, both results proved that presence of ZnO contributes to the improvement of physical properties.

The influence of ZnO on NRL vulcanisation was further demonstrated in *Figure 5*, whereby additional amounts of ZnO content slightly affected the formation of crosslinks. Even though there was hardly any significant differences in the crosslinks formed, the role of ZnO however could not be neglected. Thus, it is interesting to note that the residual DEC reduced with increase of ZnO, as shown in *Figure 6*. When ZnO was added into the latex formulation, higher crosslink densities developed. As indicated before, the additional presence of Zn atoms ensured rapid crosslink reactions and created a denser network, thereby restricting the elution of residual DEC. The presence of ZnO proved its contribution to the formation of denser crosslinks; hence improving the physical properties besides minimizing the elution of residual DEC.

The exposure of NRL films at high temperatures for a prolonged period weakened and thereby destabilised the crosslink formation, due to the break of crosslinks¹⁵. The TS and M300 values of the heated NRL films are plotted in *Figure 7* and *Figure 8*.

NRL films heated at 100°C and 120°C showed a slight decrease in TS and M300, while films heated at 140°C and 160°C

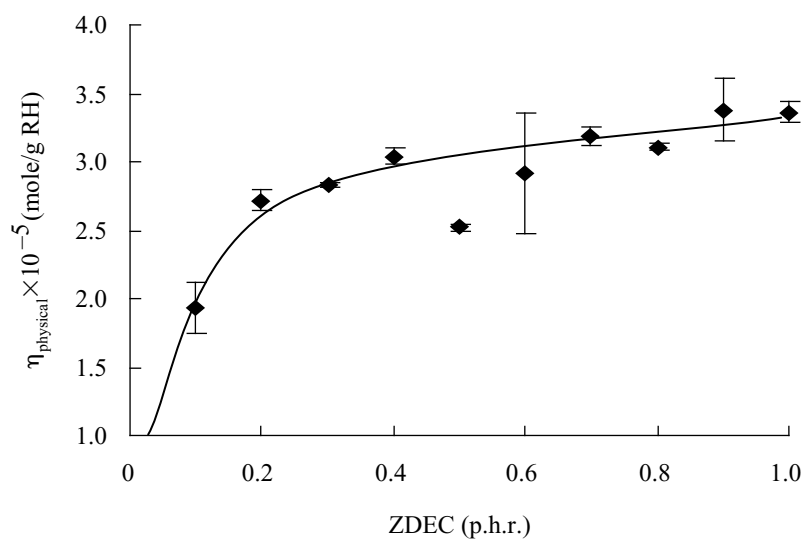


Figure 2. Effect of varied ZDEC content to crosslink density.

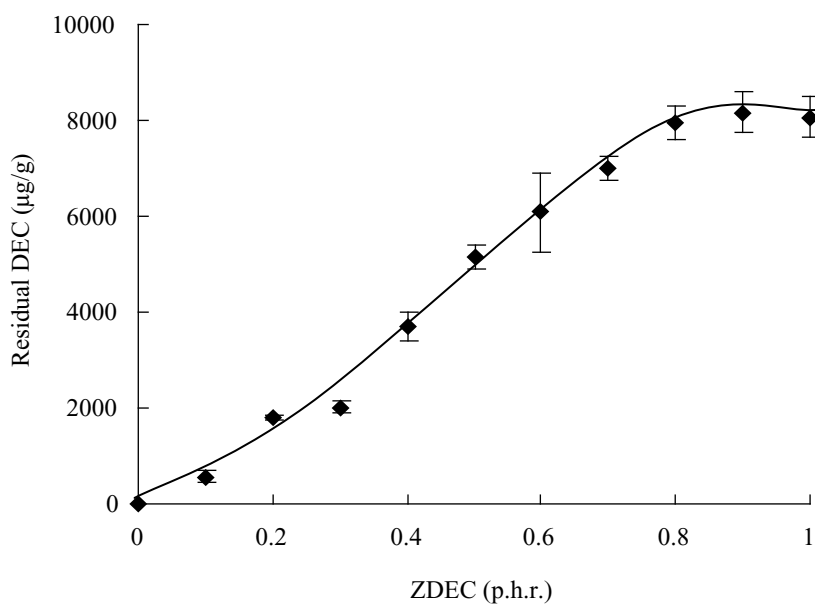


Figure 3. Residual DEC against varied ZDEC content.

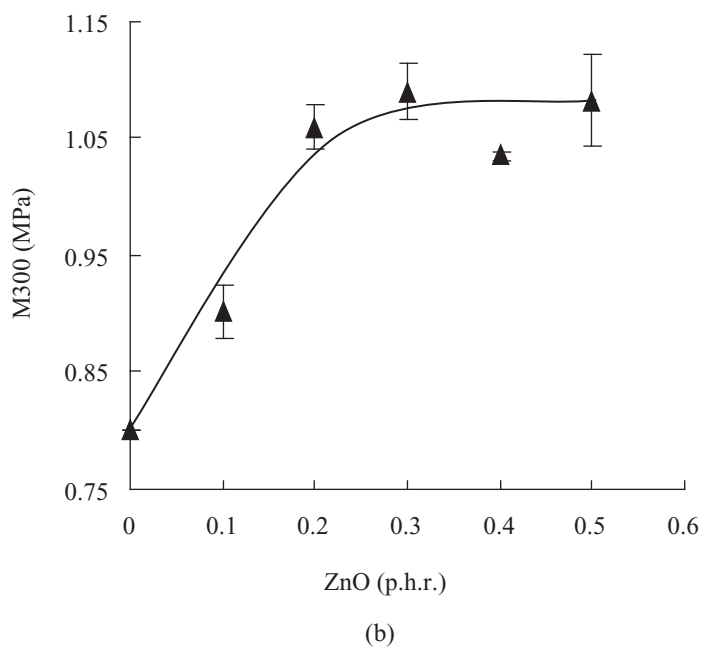
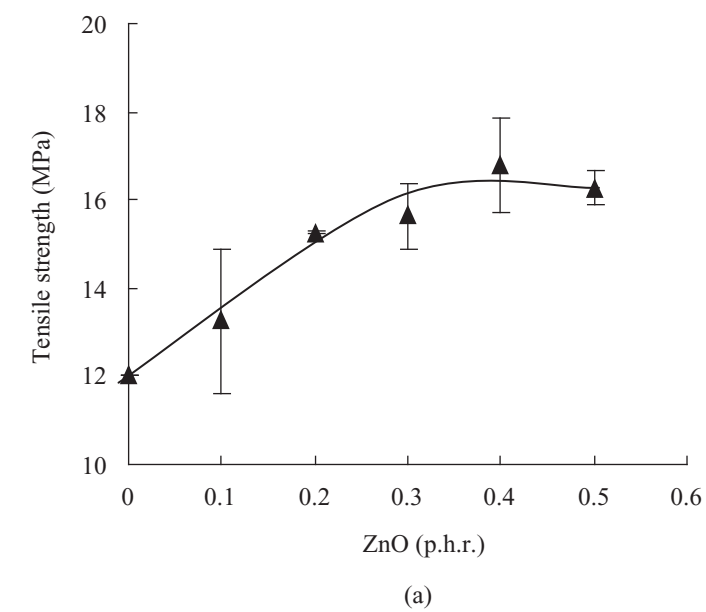


Figure 4. Effect of varied ZnO to (a) TS values and (b) M300 values.

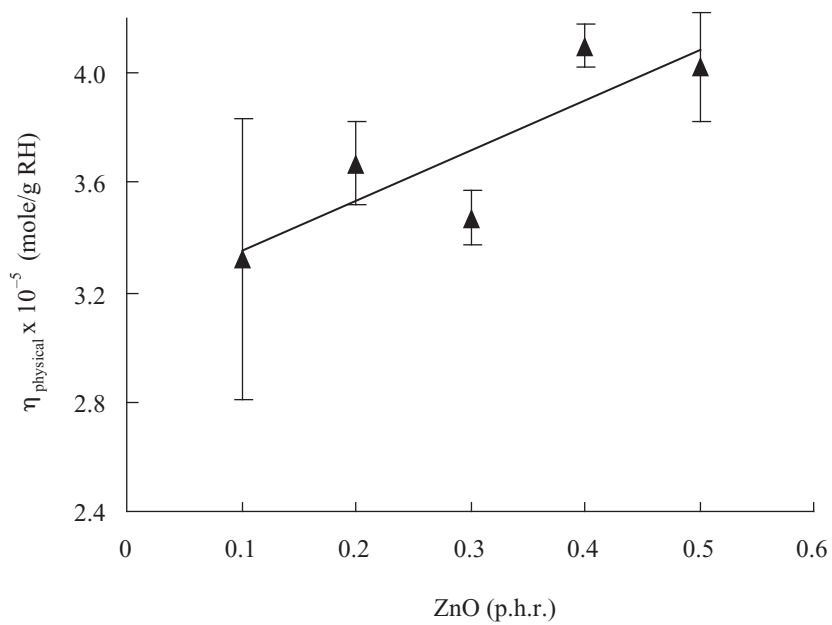


Figure 5. Effect of varied ZnO to the formation of crosslink density.

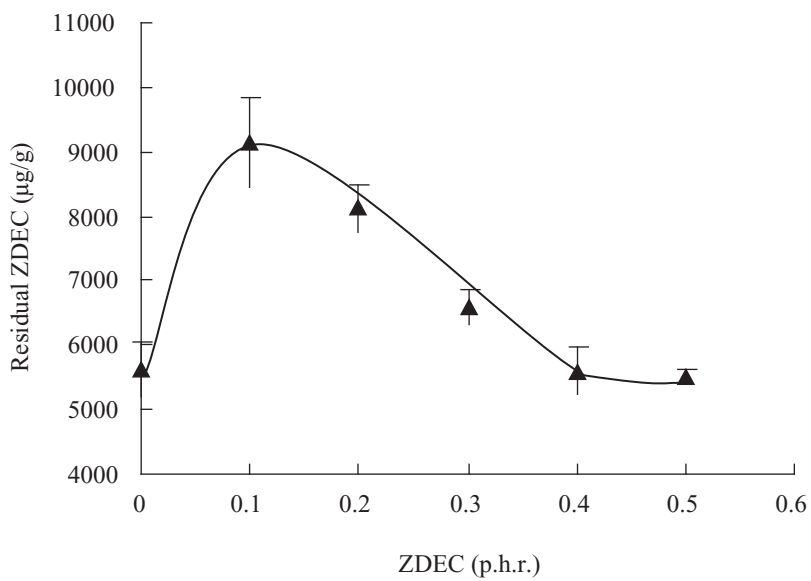


Figure 6. Residual DEC against varied ZnO.

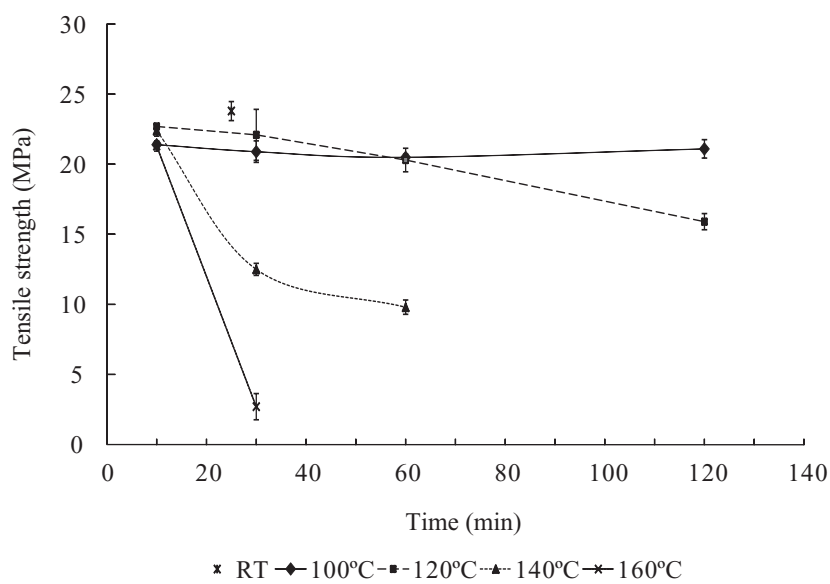


Figure 7. Effect of temperature on tensile strength at prolong heat exposure.

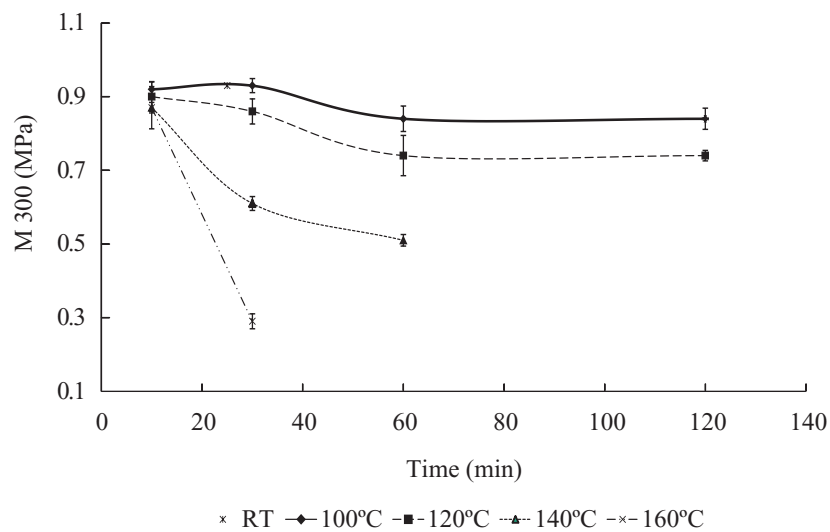


Figure 8. Effect of temperature on M300 with prolonged heat exposure.

experienced drastic reductions in properties, probably due to the decomposition of the polysulphidic crosslinks. This decomposition forms various hydrocarbons and cyclic groups in the main polymer chains and these groups are considered to be unstable and provide a high possibility of the NRL film rupture. Even though the TS values for films heated below 120°C reduced upon longer heating times, the M300 remained of plateau, even after 60 min of heating. NRL films heated for 10 min were able to maintain comparable TS and M300 values, even though being exposed up to 160°C. This showed that a very much relatively short heat exposure did not affect the strength properties of these NRL films.

As indicated earlier, sulphur vulcanisation generates mainly a carbon-sulphur-carbon

type crosslink network. Theoretically, heat induced to the NRL films would be transformed to activation energy, thus causing thermal instability to the polymer backbone. In accordance to that, desulphuration of carbon-sulphur-carbon would occur in which sulphur atoms are progressively decomposed to mainly carbon-sulphur (monosulphide) crosslinks¹⁶. Therefore, *Figure 9* shows the deterioration of crosslinks after being exposed at elevated temperatures. Nevertheless, this was not observed at temperatures of 120°C or less. It was found that the initial heating up to 10 min was still able to maintain adequate crosslink density. Decomposition of the polysulphides became significant once the desulphuration begin. The decomposition of polysulphide crosslinks is considered to be the main

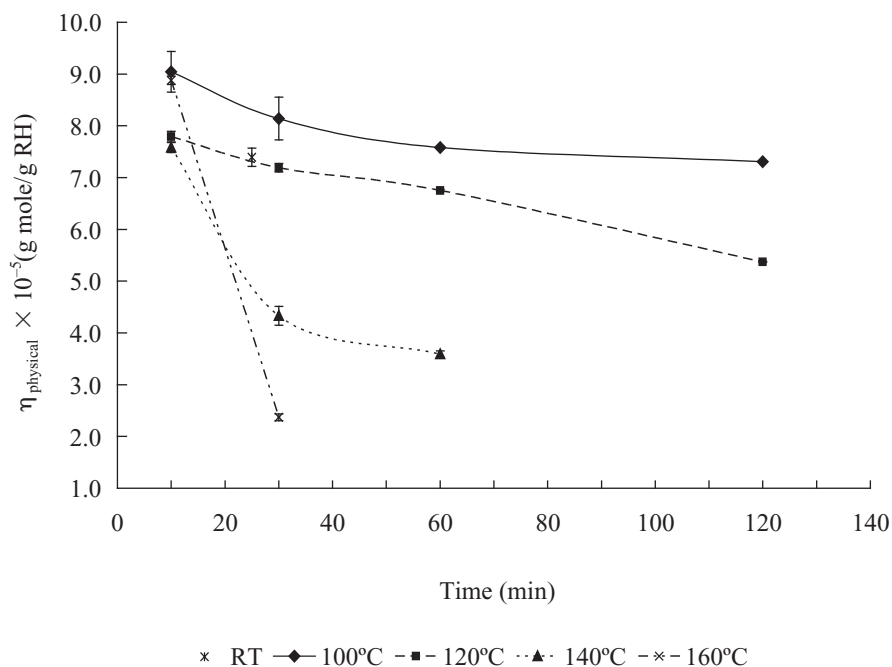


Figure 9. Effect of temperature and heating time to the crosslink formations.

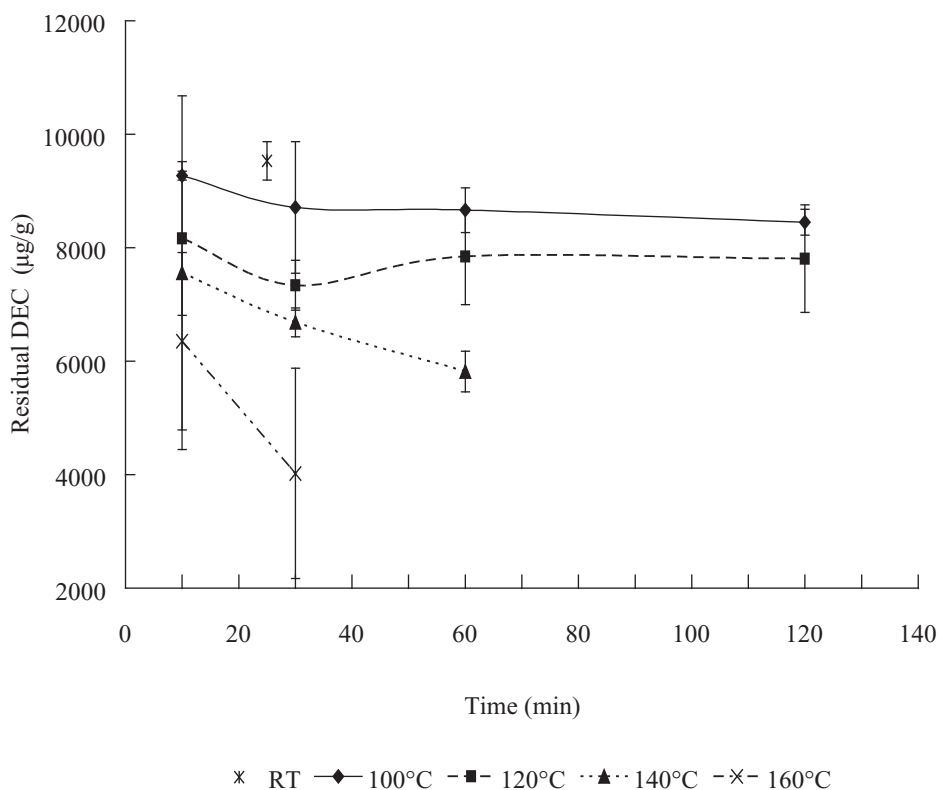


Figure 10. Effect of heating temperatures on the residual DEC.

reason for the reduction in crosslink density especially at temperatures higher than 120°C.

Heating the NRL films apparently reduced the crosslink density, affecting the physical properties and also the residual DEC, as illustrated in *Figure 10*. Heating NRL films at 140°C and 160°C possessed much less DEC when compared to films after being heated at 100°C and 120°C. The reduction in DEC was found to be between 10%–30% with an increase of temperature and time. In the present study, it was demonstrated that

exposing NRL films to heat resulted in less residual DEC being available for elution as compared to non-heated films.

CONCLUSIONS

In producing NRL films, suggestion to utilise 0.8–0.9 p.h.r. ZDEC with 0.3–0.4 p.h.r. ZnO in the presence of 1.0 p.h.r. sulphur could be considered in latex formulation, to obtain NRL films with acceptable physical properties with minimum residual DEC. Prolonged heat exposure to NRL films should be put into practice. It was found that films

heated at 120°C or less up to 60 min reduced the residual DEC without giving significant differences in physical performances of the NRL films.

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